

## Process for Coating Particulates with Phosphated Castor Oil

### Field of the Invention

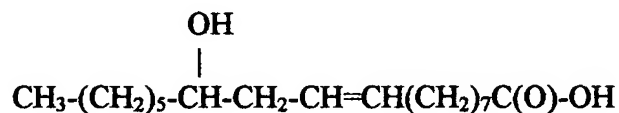
[001] The present invention relates to a process for coating particulates with a phosphated derivative of castor oil or hydrogenated castor oil as well as phosphated esters of ricinoleic acid. The inclusion of the phosphate group results in improved water solubility and a series of dispersants and emulsifiers that provide excellent particulate dispersing properties. The word particulate is meant to include pigments and bismuth oxychloride, titanated mica, fumed silica, spherical silica, polymethylmethacrylate, micronized teflon, boron nitride, acrylate copolymers, aluminum silicate, aluminum starch octenylsuccinate, bentonite, calcium silicate, cellulose, chalk, corn starch, diatomaceous earth, fuller's earth, glyceryl starch, hectorite, hydrated silica, kaolin, magnesium aluminum silicate, magnesium trisilicate, maltodextrin, montmorillonite, microcrystalline cellulose, rice starch, silica, talc, mica, titanium dioxide, zinc laurate, zinc myristate, zinc rosinate, alumina, attapulgite, calcium carbonate, calcium silicate, dextran, kaolin, nylon, silica silylate, silk powder, sericite, soy flour, tin oxide, titanium hydroxide, trimagnesium phosphate, walnut shell powder, or mixtures thereof. The above mentioned powders may be surface treated with lecithin, amino acids, mineral oil, silicone oil or various other agents either alone or in combination, which coat the powder surface and render the particles more lipophilic in nature. The word processing is meant to include milling, grinding, crushing or pulverizing. The oil is added to provide a vehicle into which the particulate is placed to facilitate the processing and provide a coating of the particulate.

## Background of the Invention

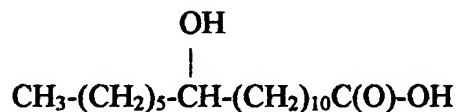
[002] Castor oil is a unique triglyceride. It is derived from *Ricinus communis* L. The castor plant grows wild in many subtropical and tropical areas. Today Brazil, China and India provide over 90% of the oil. Castor oil contains a large content of hydroxy containing compounds that are unsaturated.

[003] Castor Oil is a clear, viscous, light colored fluid that is nondrying and quite stable. The Purity of Castor Oil occurs with remarkable uniformity. Regardless of country of origin, or season it is grown, the composition and chemical properties remain within a very narrow range. Castor Oil has broad compatibility with oils, waxes, natural resins, and gums.

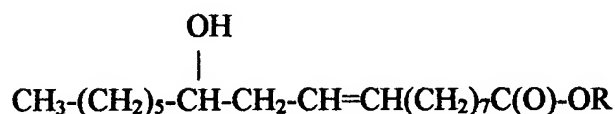
[004] Another unique aspect of castor oil is the high level of ricinoleic acid in the molecule. Castor oil contains 89% of the acid, which conforms to the following structure;



[005] When hydrogenated the double bond is lost giving hydrogenated ricinoleic, or 12-hydroxy stearic acid.

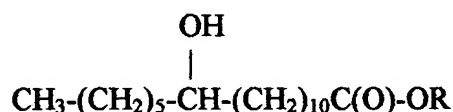


[006] When the acids derived from castor (ricinoleic acid) are reacted with alcohols having 6 to 22 carbon atoms the resulting esters are also suitable candidates for phosphorylation.



wherein R is  $\text{CH}_3-(\text{CH}_2)_n-$  and n is an integer ranging from 5 to 21.

[007] When the acids derived from hydrogenated castor (12-hydroxy-stearic acid) are reacted with alcohols having 6 to 22 carbon atoms the resulting esters are also suitable candidates for phosphorylation.



wherein R is  $\text{CH}_3-(\text{CH}_2)_n-$  and n is an integer ranging from 5 to 21.

### Summary of the Invention

[008] The present invention relates to use of a series of compounds in which the hydroxyl group in alkyl group of castor is phosphorylated, resulting in a surface-active agent that has outstanding particulate dispersing properties. Included within this definition of castor compounds are castor oil (a triglyceride), hydrogenated castor oil, ricinoleic acid and 12-hydroxystearic acid compounds. The present invention relates to a process for

processing particulate with a phosphated derivative of castor oil or hydrogenated castor oil as well as phosphated esters of ricinoleic acid. The inclusion of the phosphate group results in improved water solubility and a series of dispersants and emulsifiers that provide excellent particulate dispersing properties. The word particulate is meant to include bismuth oxychloride, titanated mica, fumed silica, spherical silica, polymethylmethacrylate, micronized teflon, boron nitride, acrylate copolymers, aluminum silicate, aluminum starch octenylsuccinate, bentonite, calcium silicate, cellulose, chalk, corn starch, diatomaceous earth, fuller's earth, glyceryl starch, hectorite, hydrated silica, kaolin, magnesium aluminum silicate, magnesium trisilicate, maltodextrin, montmorillonite, microcrystalline cellulose, rice starch, silica, talc, mica, titanium dioxide, zinc laurate, zinc myristate, zinc rosinate, alumina, attapulgite, calcium carbonate, calcium silicate, dextran, kaolin, nylon, silica silylate, silk powder, sericite, soy flour, tin oxide, titanium hydroxide, trimagnesium phosphate, walnut shell powder, or mixtures thereof. The above mentioned powders may be surface treated with lecithin, amino acids, mineral oil, silicone oil or various other agents either alone or in combination, which coat the powder surface and render the particles more lipophilic in nature. The word processing is meant to include milling, grinding, crushing or pulverizing. The oil is added to provide a vehicle into which the particulate is placed to facilitate the processing and provide a coating of the particulate.

[009] The invention also relates to the utilization of these phosphated materials as surface-active agents in personal care and industrial applications. These materials function as particulate wetters, and emulsifiers. As particulate wetters the compounds of the present invention coat the hydrophobic particulate making them disperse in aqueous

formulations. The compounds of the present invention have the proper balance of water loving and oil loving portions to allow for the formation of very stable particulate dispersions.

### **Objective of the Invention**

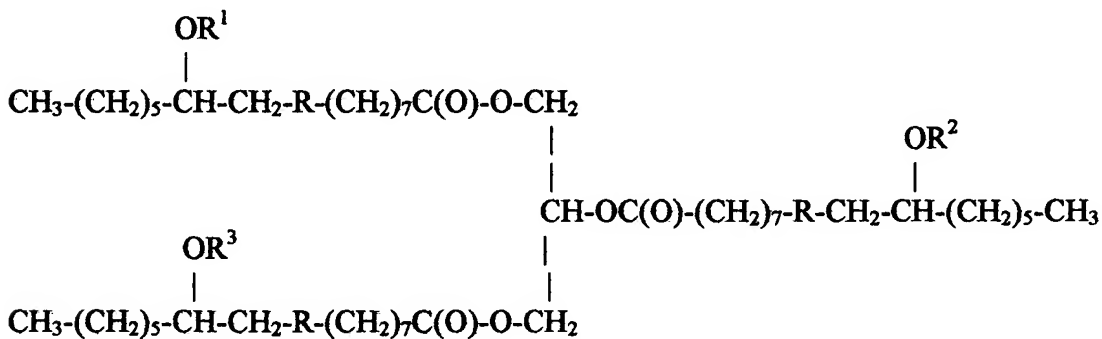
[010] It is the objective of the present invention to provide particulate wetting and dispersing agents derived from the phosphorylation of castor oil, hydrogenated castor oils or esters derived there from. The compounds are outstanding particulate dispersants. Additionally, the objective of the present invention is the utilization of the compounds of the present invention with particulates to make dispersions of outstanding stability.

### **Detailed Description of the Invention**

[011] The present invention, is a process for dispersing particulate with a phosphated derivative of castor oil or hydrogenated castor oil as well as phosphated esters of ricinoleic acid. The inclusion of the phosphate group results in improved water solubility and a series of dispersants and emulsifiers that provide excellent particulate dispersing properties. The word particulate is meant to include pigments and bismuth oxychloride, titanated mica, fumed silica, spherical silica, polymethylmethacrylate, micronized teflon, boron nitride, acrylate copolymers, aluminum silicate, aluminum starch octenylsuccinate, bentonite, calcium silicate, cellulose, chalk, corn starch, diatomaceous earth, fuller's earth, glyceryl starch, hectorite, hydrated silica, kaolin, magnesium aluminum silicate, magnesium trisilicate, maltodextrin, montmorillonite, microcrystalline cellulose, rice

starch, silica, talc, mica, titanium dioxide, zinc laurate, zinc myristate, zinc rosinate, alumina, attapulgite, calcium carbonate, calcium silicate, dextran, kaolin, nylon, silica silylate, silk powder, sericite, soy flour, tin oxide, titanium hydroxide, trimagnesium phosphate, walnut shell powder, or mixtures thereof. The above mentioned powders may be surface treated with lecithin, amino acids, mineral oil, silicone oil or various other agents either alone or in combination, which coat the powder surface and render the particles more lipophilic in nature. The word processing is meant to include milling, grinding, crushing or pulverizing. The oil is added to provide a vehicle into which the particulate is placed to facilitate the processing and provide a coating of the particulate. castor oil is phosphated using poly phosphoric acid (PPA). The resulting product ranges from water dispersible, when only one of the three hydroxyl groups is phosphated, to water soluble when all three are phosphated.

[012] The present invention is directed toward a process for dispersing particulates which comprises mixing a phosphated triglyceride conforming to the following structure



wherein;

R is selected from the group consisting of  $-(CH_2)_2-$  and  $-CH-CH-$ ;

$R^1$  is  $-P(O)-(OH)_2$

$R^2$  and  $R^3$  are independently selected from the group consisting of H and  $-P(O)-(OH)_2$

with a particulate selected from the group consisting of bismuth oxychloride, titanium

dioxide, zinc oxide, ferric oxide, ferric titanated mica, fumed silica, spherical silica,

polymethylmethacrylate, micronized teflon, boron nitride, acrylate copolymers,

aluminum silicate, aluminum starch octenylsuccinate, bentonite, calcium silicate,

cellulose, chalk, corn starch, diatomaceous earth, fuller's earth, glyceryl starch, hectorite,

hydrated silica, kaolin, magnesium aluminum silicate, magnesium trisilicate,

maltodextrin, montmorillonite, microcrystalline cellulose, rice starch, silica, talc, mica,

titanium dioxide, zinc laurate, zinc myristate, zinc rosinate, alumina, attapulgite, calcium

carbonate, calcium silicate, dextran, kaolin, nylon, silica silylate, silk powder, sericite,

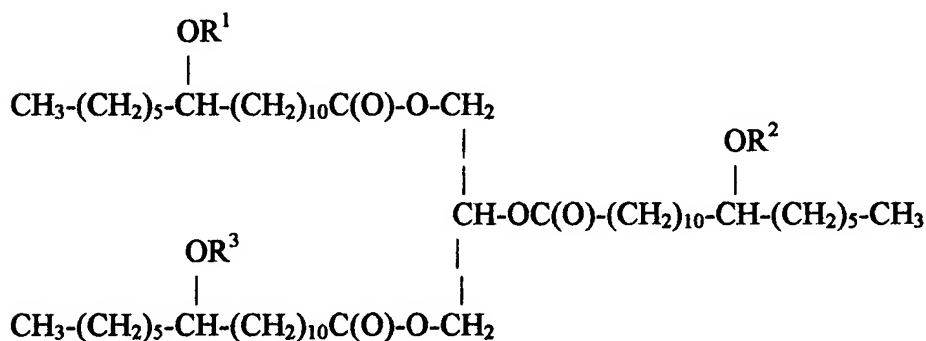
soy flour, tin oxide, titanium hydroxide, trimagnesium phosphate, walnut shell powder, or

mixtures thereof and optionally milling, grinding, or homogenizing the mixture to obtain

the desired particle size.

[013] One subset set of the generic set compounds used in the process of the present

invention conforms to the following structure based upon hydrogenated castor oil;

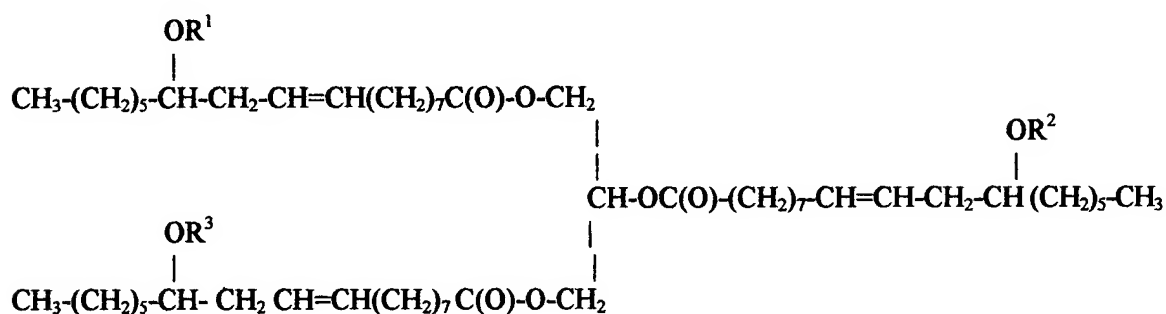


wherein;

$R^1$  is  $-P(O)-(OH)_2$

$R^2$  and  $R^3$  are independently selected from the group consisting of H and  $-P(O)-(OH)_2$ .

[014] Another subset of compounds useful in the process of the present invention is based upon castor oil and conforms to the following structure;

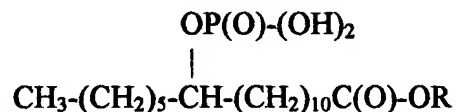


wherein;

$R^1$  is  $-P(O)-(OH)_2$

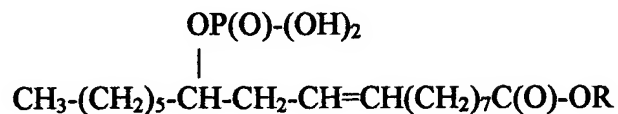
$R^2$  and  $R^3$  are independently selected from the group consisting of H and  $-P(O)-(OH)_2$ .

[015] Another set of compounds useful in the process of the present invention conform to the following structure;



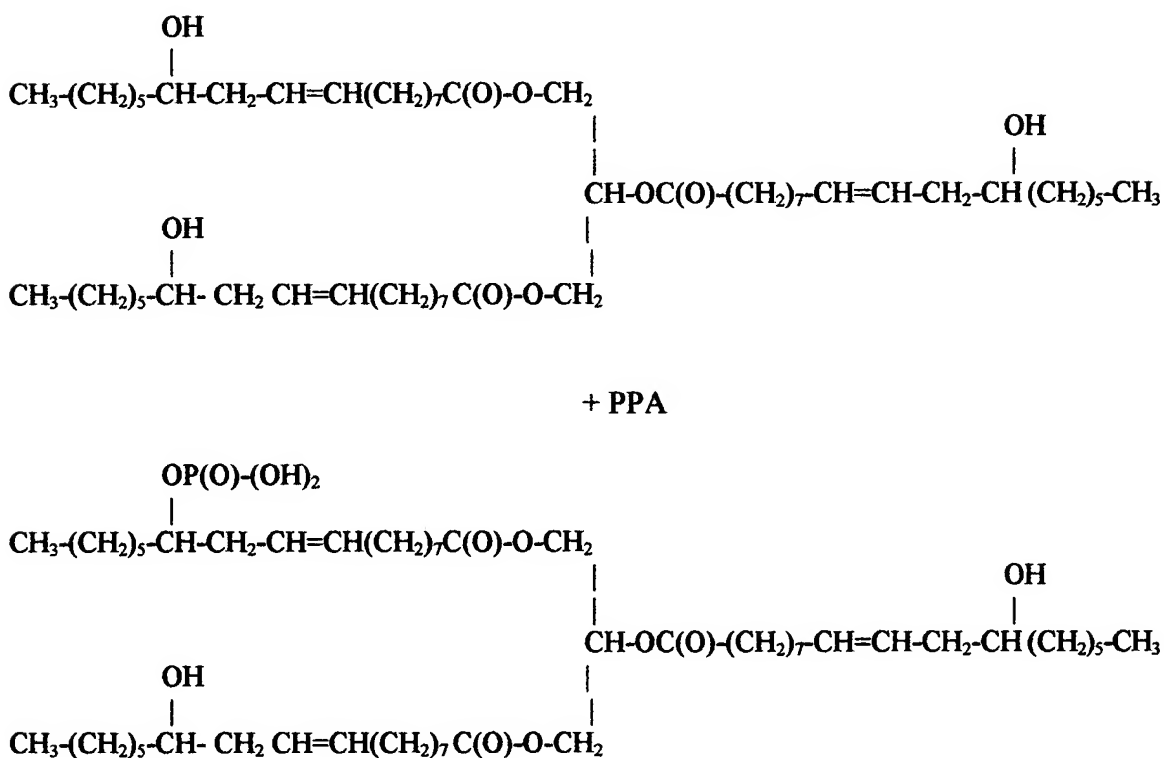


[016] Finally, another set of compounds useful in the process of the present invention conforms to the following structure;

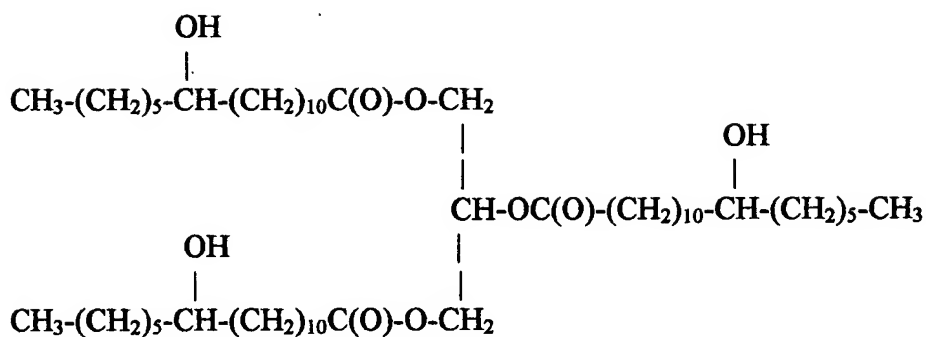


wherein R is  $\text{CH}_3\text{-(CH}_2)_n\text{-}$  and n is an integer ranging from 5 to 21.

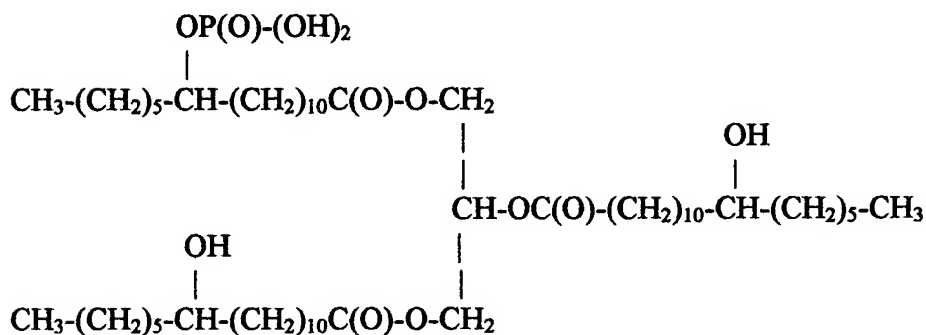
[017] The reaction with castor oil is as follows;



[018] The reaction for the hydrogenated castor is identical to that of the castor, except the double bond is not present. This results in a phosphated castor wax. The reaction proceeds as follows:

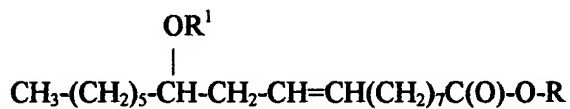


+ PPA



[019] The changing of the amount of PPA will allow for phosphating the remaining hydroxyl groups resulting in a di-phosphate ( if 2 equivalents of PPA are used), or a

[020] Phosphated ricinoleic acid ester conform to the following structure



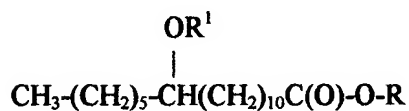
wherein;

R is  $-(\text{CH}_2)_n-\text{CH}_3$

R<sup>1</sup> is  $-\text{P}(\text{O})-(\text{OH})_2$

n is an integer ranging from 5 to 21.

[021] Phosphated 12-hydroxy stearic acid esters conform to the following structure



wherein;

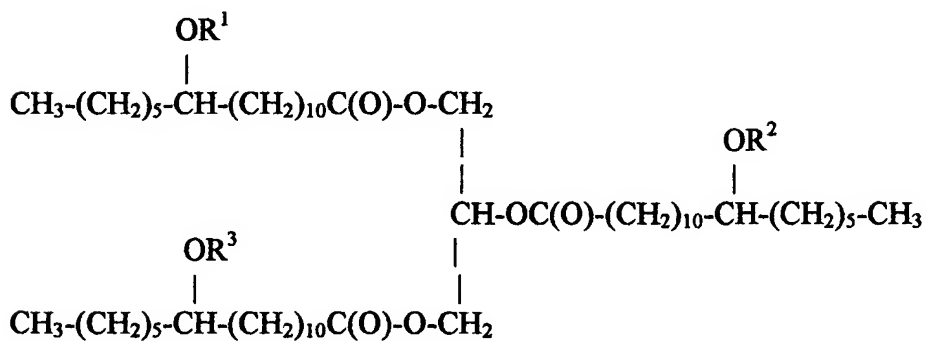
R is  $-(\text{CH}_2)_n-\text{CH}_3$

R<sup>1</sup> is  $-\text{P}(\text{O})-(\text{OH})_2$

n is an integer ranging from 5 to 21

### Preferred Embodiments

[022] In a preferred embodiment the phosphated compounds belong to class 1 and conforming to the following structure;



wherein;

R<sup>1</sup> is  $-\text{P}(\text{O})-(\text{OH})_2$

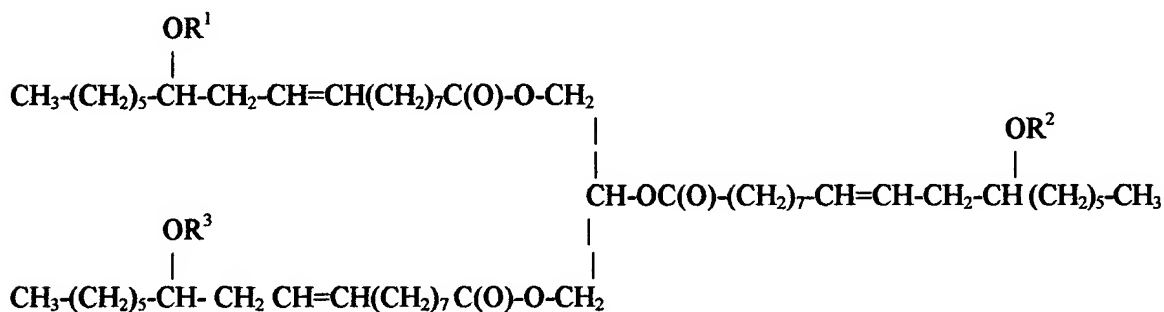
R<sup>2</sup> and R<sup>3</sup> are independently selected from the group consisting of H and  $-\text{P}(\text{O})-(\text{OH})_2$ .

[023] In a preferred embodiment of class 1  $R^2$  and  $R^3$  are H.

[024] In a preferred embodiment of class 1  $R^2$  is  $-P(O)-(OH)_2$  and  $R^3$  is H.

[025] In a preferred embodiment of class 1  $R^2$  and  $R^3$  are both  $-P(O)-(OH)_2$

[026] In a preferred embodiment of class 2 the phosphated compound conforming to the following structure



wherein;

$R^1$  is  $-P(O)-(OH)_2$

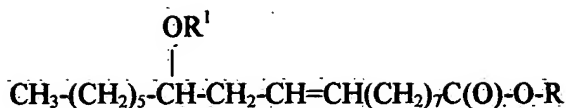
$R^2$  and  $R^3$  are independently selected from the group consisting of H and  $-P(O)-(OH)_2$ .

[027] In a preferred embodiment of class 2  $R^2$  and  $R^3$  are H.

[028] In a preferred embodiment of class 2  $R^2$  is  $-P(O)-(OH)_2$  and  $R^3$  is H.

[029] In a preferred embodiment of class 2  $R^2$  and  $R^3$  are both  $-P(O)-(OH)_2$

[030] In a preferred embodiment of class 3 the phosphated compound conforming to the following structure;



wherein;

R is  $-(\text{CH}_2)_n-\text{CH}_3$

R<sup>1</sup> is  $-\text{P}(\text{O})-(\text{OH})_2$

n is an integer ranging from 5 to 21.

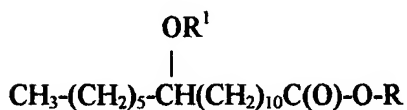
[031] In a preferred embodiment of class 3 n is 5.

[032] In a preferred embodiment of class 3 n is 11.

[033] In a preferred embodiment of class 3 n is 17.

[034] In a preferred embodiment of class 3 n is 21.

[035] In a preferred embodiment of class 4 the phosphated compound conforming to the following structure



wherein;

R is  $-(\text{CH}_2)_n-\text{CH}_3$ ;

R<sup>1</sup> is  $-\text{P}(\text{O})-(\text{OH})_2$ ;

n is an integer ranging from 5 to 21.

[036] In a preferred embodiment of class 3 n is 5.

[037] In a preferred embodiment of class 3 n is 11.

[038] In a preferred embodiment of class 3 n is 17.

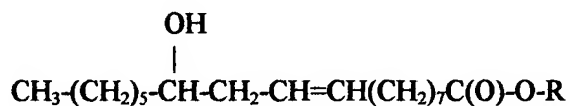
[039] In a preferred embodiment of class 3 n is 21.

### Examples

[040] Castor oil is an item of commerce and is commercially available from a variety of sources including the Fanning Corporation of Chicago Il.

[041] Polyphosphoric Acid is an item of commerce and is sometimes called 115% phosphoric acid.

[042] Ricinoleic esters are items of commerce and are commercially available from Phoenix Chemical, Somerville, N.J.. They conform to the following structure:



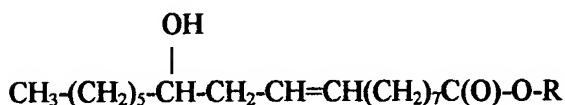
wherein;

R is  $-(\text{CH}_2)_n-\text{CH}_3$

n is an integer ranging from 5 to 21

Example	n
Raw Material 1	5
Raw Material 2	11
Raw Material 3	17
Raw Material 4	21

[043] 12-hydroxy stearic acid esters are items of commerce and are commercially available from Phoenix Chemical, Somerville, N.J.. They conform to the following structure:



R is  $-(\text{CH}_2)_n-\text{CH}_3$

n is an integer ranging from 5 to 21.

Example	n
Raw Material 5	5
Raw Material 6	11
Raw Material 7	17
Raw Material 8	21

### Phosphating Agents

[044] Polyphosphoric Acid (PPA) is 115 % phosphoric acid. The phosphates of this invention can be prepared by reacting the hydroxyl containing with a suitable Polyphosphoric acid. It will be understood that the product of phosphation, is a mixture of mono and di-ester.

[045] The following examples further illustrate the objects and advantages of this invention, though it should be understood that the various reactants and amounts thereof,

reaction conditions, and other details are merely illustrative and should not be construed to unduly limit this invention.

### **General Procedure**

[046] The specified amount of castor derivative is added to a suitable reaction vessel. The specified amount of polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

[047]      **Example 1**              Castor Oil Product  
(only one hydroxyl group on the triglyceride phosphated)

939.0 grams of castor oil is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

[048]      **Example 2**              Castor Oil Product  
(two of the three hydroxyl groups on the triglyceride phosphated)

626.6 grams of castor oil is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.



**[049] Example 3** Castor Oil Product  
(all three hydroxyl groups on the triglyceride phosphated)

313.3 grams of castor oil is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[050] Example 4** Hydrogenated Castor Oil Product  
(only one hydroxyl group on the triglyceride phosphated)

933.0 grams of hydrogenated castor oil is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[051] Example 5** Hydrogenated Castor Oil Product  
(two of the three hydroxyl groups on the triglyceride phosphated)

622.0 grams of hydrogenated castor oil is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[052] Example 6 Hydrogenated Castor Oil Product**  
(all three hydroxyl groups on the triglyceride phosphated)

311.0 grams of hydrogenated castor oil is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[053] Example 7**

522.5 grams of castor oil is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[054] Example 8 Ricinoleic Esters**

800.0 grams of ricinoleic ester Raw Material Example 1 is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[055] Example 9**

972.0 grams of ricinoleic ester Raw Material Example 2 is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[056] Example 10**

1320.0 grams of ricinoleic ester Raw Material Example 3 is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[057] Example 11 Ricinoleic Ester**

1600.0 grams of ricinoleic ester Raw Material Example 4 is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the

mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[058] Example 12** 12-hydroxy-stearic ester

802.0 grams of 12-hydroxy stearic ester Raw Material Example 5 is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[059] Example 13** 12-hydroxy-stearic ester

1010.0 grams of 12-hydroxy stearic ester Raw Material Example 6 is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[060] Example 14** 12-hydroxy-stearic ester

1410.0 grams of 12-hydroxy stearic ester Raw Material Example 7 is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation

over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[061] Example 15                      12-hydroxy-stearic ester**

666.6 grams of 12-hydroxy stearic ester Raw Material Example 8 is added to a suitable reaction vessel. The 114 grams of Polyphosphoric acid is charged to under good agitation over a 2 hr. period, under good agitation. The exothermic reaction raises the temperature of the mixture to about 70 C. After 1 hour slowly raise the temperature to 100 C and hold 2 - 4 hours.

**[062] Applications Examples**

**[063]** The compounds of the present invention examples 1-15 are water dispersible to varying extents depending upon the percentage of phosphate in the molecule. The lower the amount of phosphate in the molecule the more castor oil soluble the product. The higher the amount of the phosphate present the more water-soluble the product. The compounds make very efficient emulsifiers. Low percentage phosphate products favor water in oil emulsions, the higher the level of phosphate favor oil in water emulsions.

**[064]** The compounds of the present invention are also very efficient particulate dispersants. The particulates used in color cosmetics are ground into low particle size in an oil phase. The phosphated products of the present invention allow for effective

